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(54) **SUBSTITUTED PYRAZOLYLPIRAZOLE
DERIVATIVE AND USE OF SAME AS
HERBICIDE**

(71) Applicant: **KYOYU AGRI CO., LTD.**, Kanagawa
(JP)

(72) Inventors: **Ken Matsubara**, Nagano (JP); **Makoto
Niino**, Nagano (JP)

(73) Assignee: **KYOYU AGRI CO., LTD.**, Kanagawa
(JP)

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(58) **Field of Classification Search**
None
See application file for complete search history.

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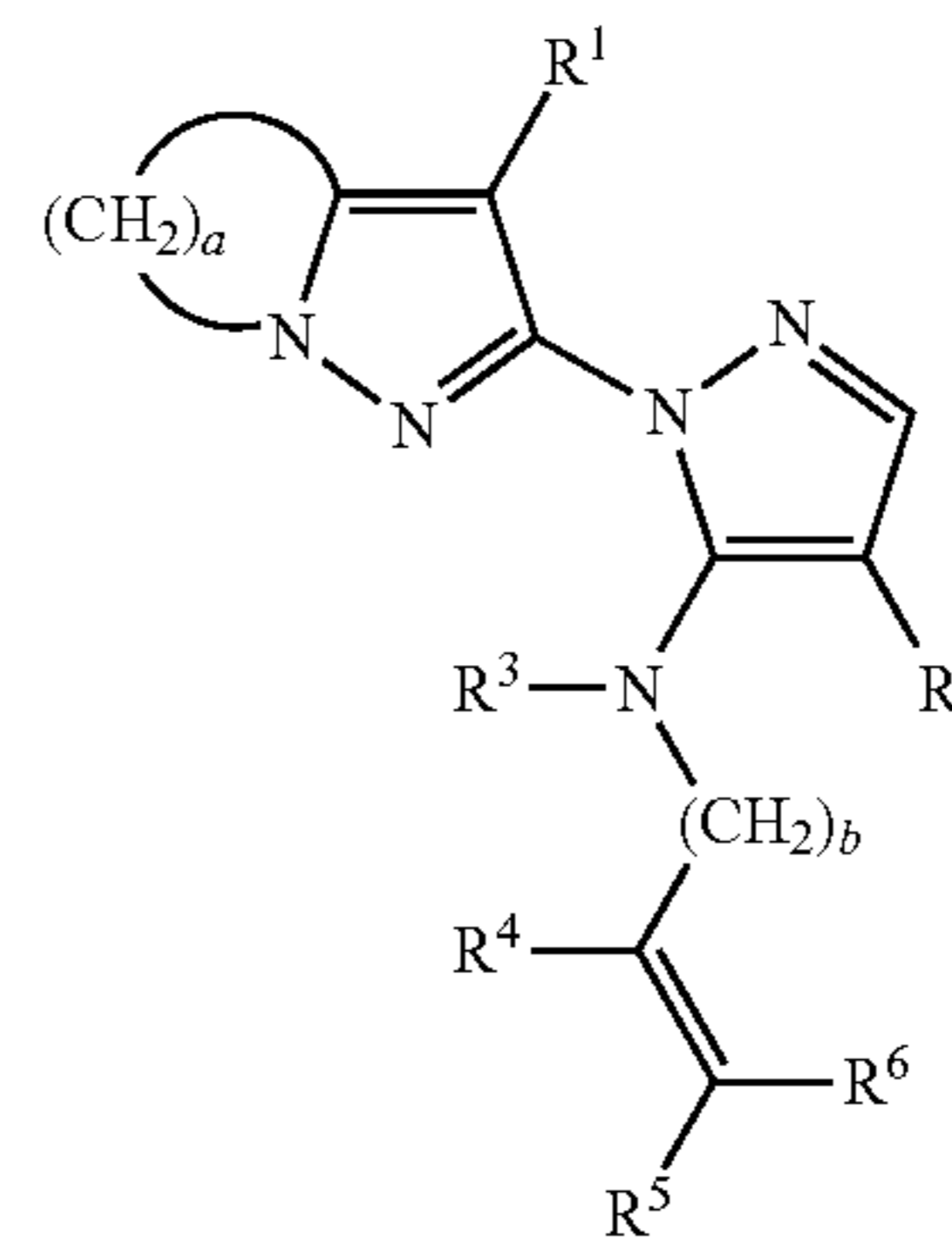
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no Zasso to Josozai Kaisetsu (Ecology of Paddy Weeds and their
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Primary Examiner — Kamal Saeed

(74) *Attorney, Agent, or Firm* — Wenderoth, Lind &
Ponack, L.L.P.

(57) **ABSTRACT**

Provided is a compound capable of effectively control worst
weeds of higher leaf stages that present practical problems.
A specific pyrazolylpyrazole derivative of formula (1) is
disclosed that is able to solve the above-mentioned prob-
lems.



18 Claims, No Drawings

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**SUBSTITUTED PYRAZOLYLPIRAZOLE
DERIVATIVE AND USE OF SAME AS
HERBICIDE**

TECHNICAL FIELD

The present invention relates to a substituted pyrazolylpyrazole derivative and the use of that compound as an herbicide.

BACKGROUND ART

Numerous herbicides have recently come to be used in the cultivation of agricultural crops, and have contributed to reduced labor for farmers and improved productivity of agricultural crops. Numerous herbicides are also used practically in the cultivation of field and paddy rice.

However, there is considerable diversity in the species of weeds, the germination and growth periods of each species of weed are not uniform, and the growth of perennial weeds extends over a long period of time. Consequently, it is extremely difficult to control all weeds with a single spraying of herbicide.

Early to mid-term one-shot herbicides have been shown to be effective for paddy rice by treating during the second to third leaf stage of paddy weeds (generic term for *Echinochloa oryzicola*, *Echinochloa crus-galli* var. *crus-galli*, *Echinochloa crus-galli* var. *formosensis*, *Echinochloa crus-galli* var. *praticola* and *Echinochloa crus-galli* var. *caudata*), and major weeds can be controlled by a single treatment (see Non-Patent Document 1). However, it is extremely difficult to control paddy weeds that have grown to the 3.5 leaf stage or more with early to mid-term one-shot herbicides currently in practical use, and the control of paddy weeds in the third leaf stage and control of paddy weeds in the 3.5 leaf stage are technically completely different.

Moreover, maintaining herbicidal effects (residual activities) over a long period of time is important in terms of reducing spraying of agricultural chemicals, saving on labor and curtailing costs, and is considered to be an essential area of performance for early to mid-term one-shot herbicides.

In addition, acetolactate synthase (ALS) inhibitors have come to be widely used in recent years, and weeds exhibiting resistance to ALS inhibitors have become a problem. There are few herbicides demonstrating adequate efficacy against ALS inhibitor-resistant biotypes of the perennials of *Sagittaria trifolia* and *Sagittaria pygmaea*. In addition, examples of perennial weeds that have caused problems in recent years include *Eleocharis kuroguwai*, *Scirpus planiculmis* and *Scirpus nipponicus*, while examples of annuals include *Aeschynomene indica*, *Leptochloa chinensis* and *Murdannia keisak*, and there are few herbicides that demonstrate adequate efficacy against these difficult-to-control weeds.

On the other hand, numerous pyrazole derivatives are used practically as herbicides, and although pyrazole derivatives such as 4-(2,4-dichlorobenzoyl)-1,3-dimethyl-5-pyrazolyl p-toluenesulfonate (common name: "Pyrazolate"), 2-[4-(2,4-dichlorobenzoyl)-1,3-dimethylpyrazol-5-yloxy] acetophenone (common name: "Pyrazoxyfen") or 2-[4-(2,4-dichloro-m-toluoyl)-1,3-dimethylpyrazol-5-yloxy]-4'-methylacetophenone (common name: "Benzofenap") are widely used, their registered application range for paddy weeds in Japan when used alone is up to the 1.5 leaf stage, and although these pyrazole derivatives are effective against

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a wide range of weeds, the efficacy thereof is not always adequate against paddy weeds of higher leaf stages.

In addition, although Compound 73 of Example 4 described in Patent Document 1 in the form of 1-(3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridin-2-yl) 5-[methyl(prop-2-ynyl)amino]pyrazole-4-carbonitrile (common name: "Pyraclozil") is effective against a wide range of weeds, its efficacy against paddy weeds of higher leaf stages is inadequate, and the registered application range in Japan against paddy weeds when using this herbicide alone is up to the 1.5 leaf stage.

CITATION LIST

Patent Literature Document

Patent Document 1: WO 94/08999

Non-Patent Literature Document

Non-Patent Document 1: "Suiden Zasso no Seitai to Sono Bojo-Suitosaku no Zasso to Josozai Kaisetsu (Ecology of Paddy Weeds and their Control—Explanation of Weeds of Rice Paddy Crops and Herbicide)", p. 159

SUMMARY OF THE INVENTION

Technical Problem

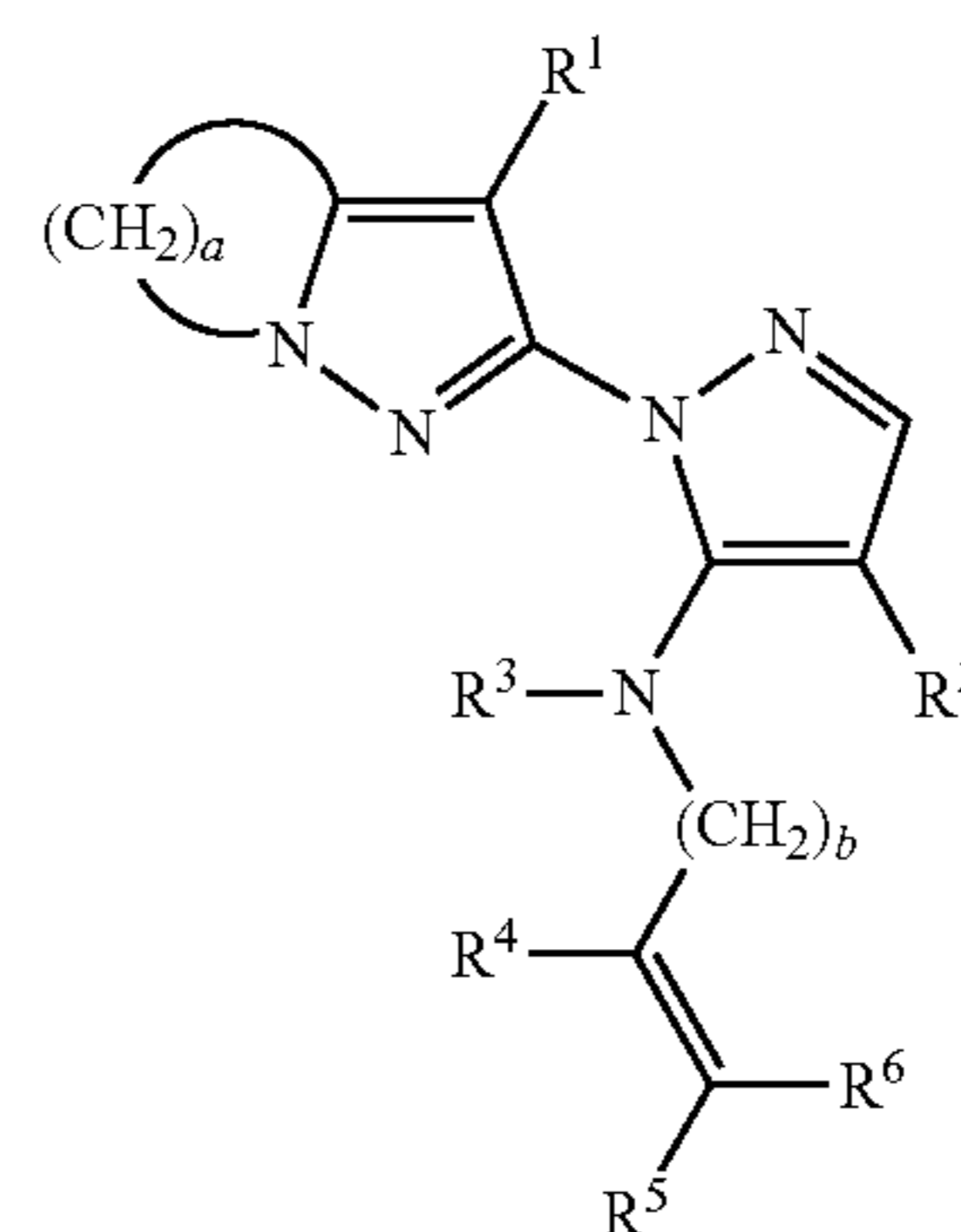
An object of the present invention is to provide a herbicide composition that has a wide herbicidal spectrum, is able to control worst weeds of higher leaf stages that present practical problems, and not cause phytotoxicity to crops such as paddy rice.

Solution Problem

As a result of conducting extensive studies to achieve the aforementioned object, the inventors of the present invention found that a pyrazolylpyrazole derivative having a specific chemical structure exhibits a wide herbicidal spectrum over a long period of time, demonstrates superior herbicidal efficacy against worst weeds of higher leaf stages, and has adequate safety with respect to cultivated crops, thereby leading to completion of the present invention on the basis of these findings.

A compound represented by the following formula (I):

[Chemical formula 1]



(I)

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wherein,

R¹ represents a halogen atom,

R² represents a cyano group or nitro group,

R³ represents a hydrogen atom, trifluoroacetyl group, pentafluoropropionyl group or heptafluorobutenyl group,

R⁴-R⁶ may be the same or different and represent hydrogen atoms, halogen atoms, C₁-C₆ alkyl groups (which may be substituted with one or more halogen atoms depending on the case), C₃-C₆ cycloalkyl groups (which may be substituted with one or more halogen atoms depending on the case), C₁-C₆ alkoxy(C₁-C₆)alkyl groups (which may be substituted with one or more halogen atoms depending on the case) or phenyl groups (which may be substituted with one or more halogen atoms, nitro groups, cyano groups, C₁-C₄ alkyl groups (which may be substituted with one or more halogen atoms depending on the case) or C₁-C₄ alkoxy groups),

a represents 3 to 5, and

b represents 0 to 2

(excluding compounds in which R¹ represents a chlorine atom, R² represents a cyano group, R³-R⁶ represent hydrogen atoms and b is 1).

Preferably,

in formula (I),

R¹ represents a chlorine atom or bromine atom,

R⁴-R⁶ may be the same or different and represent hydrogen atoms, halogen atoms, C₁-C₆ alkyl groups (which may be substituted with one or more halogen atoms depending on the case), C₃-C₆ cycloalkyl groups, C₃-C₆ alkoxy(C₁-C₆)alkyl groups or phenyl groups, and

a represents 4.

More preferably,

in formula (I),

R¹ represents a chlorine atom,

R² represents a cyano group,

R⁴-R⁶ may be the same or different and represent hydrogen atoms, halogen atoms or C₁-C₆ alkyl groups (which may be substituted with one or more halogen atoms depending on the case), and

b represents 1.

In the present description,

a description in the manner of the previous "C_a-C_b" of each substituent refers to the number of carbon atoms respectively present in that group being from a to b.

Fluorine atoms, chlorine atoms, bromine atoms and iodine atoms are included in "halogen atoms".

An "alkyl group" can be linear or branched, and although there are no limitations thereon, examples thereof include methyl, ethyl, n- or iso-propyl, n-, iso-, sec- or tert-butyl, n-pentyl and n-hexyl groups, and each is selected within a range of the specified number of carbon atoms thereof.

An "alkoxy group" refers to an alkyl-O-group in which the alkyl moiety has the above-mentioned meaning, and although there are no limitations thereon, examples thereof include methoxy, ethoxy, n- or iso-propoxy, n-, iso-, sec- or tert-butoxy groups, and each is selected within a range of the specified number of carbon atoms thereof.

Although there are no limitations on "cycloalkyl group", examples thereof include cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl groups, and each is selected within a range of the specified number of carbon atoms thereof.

In the case of the "alkyl group", "alkoxy group" and "cycloalkyl group", at least one hydrogen atom contained in these groups may be substituted with a halogen atom, and although there are no limitations thereon, examples thereof when using the example of an alkyl group include chloromethyl, dichloromethyl, trifluoromethyl, chloroethyl, dichlo-

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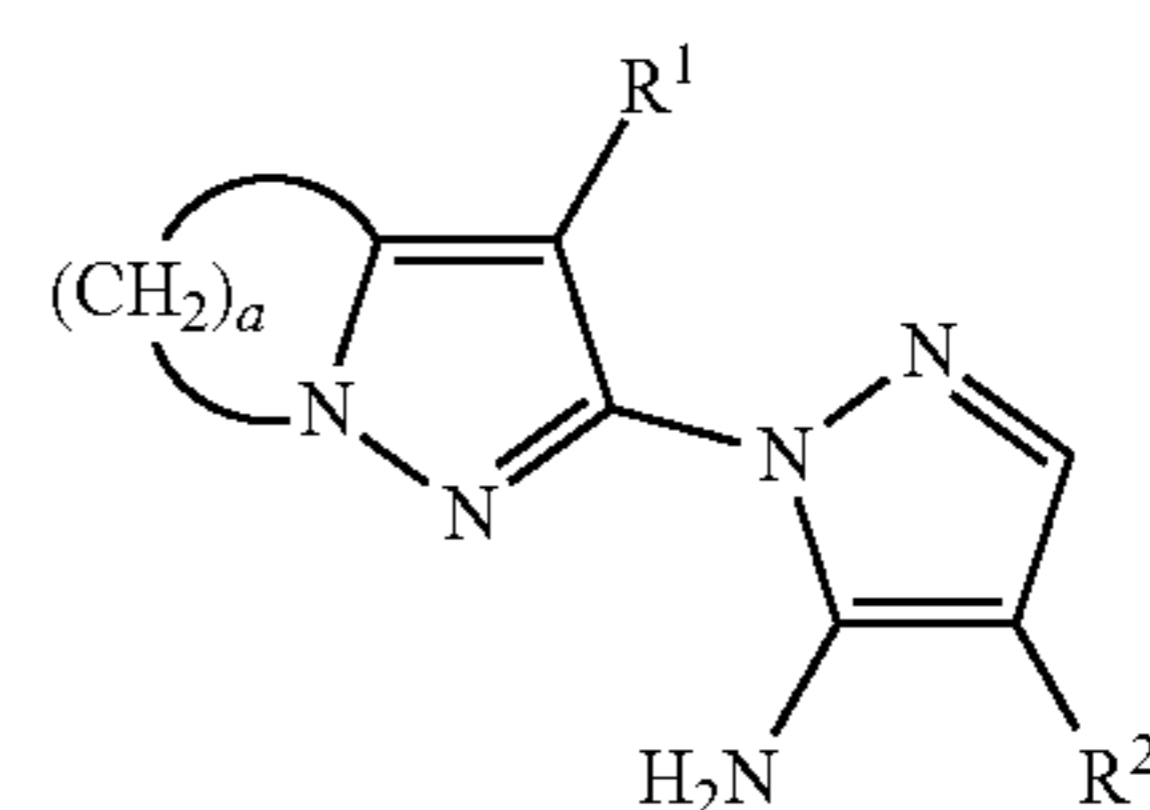
roethyl, trifluoroethyl, tetrafluoropropyl, bromoethyl, bromopropyl, chlorobutyl, chlorohexyl and perfluorohexyl groups, and each of these is selected within a range of the specified number of carbon atoms thereof.

In the case where the aforementioned group or moiety is substituted with a plurality of halogen atoms or a phenyl group is substituted with a plurality of halogen atoms, nitro groups, cyano groups, C₁-C₄ alkyl groups (which may be substituted with one or more halogen atoms depending on the case) or C₁-C₄ alkoxy groups, that group can be substituted with more than one halogen atoms and/or substituents that are the same or different.

In addition, the cis form and trans form are included in cases of the presence of geometrical isomers. Although the present invention includes compounds represented by formula (I), it also relates to all geometrical isomers and mixtures thereof not specifically defined.

In all of the formulas listed below, substituents and symbols have the same meanings as defined in formula (I) unless specifically defined otherwise. Among the compounds of formula (I) provided by the present invention, compounds in which R³ is a hydrogen atom can be easily synthesized by an alkylation reaction of a compound represented by formula (II).

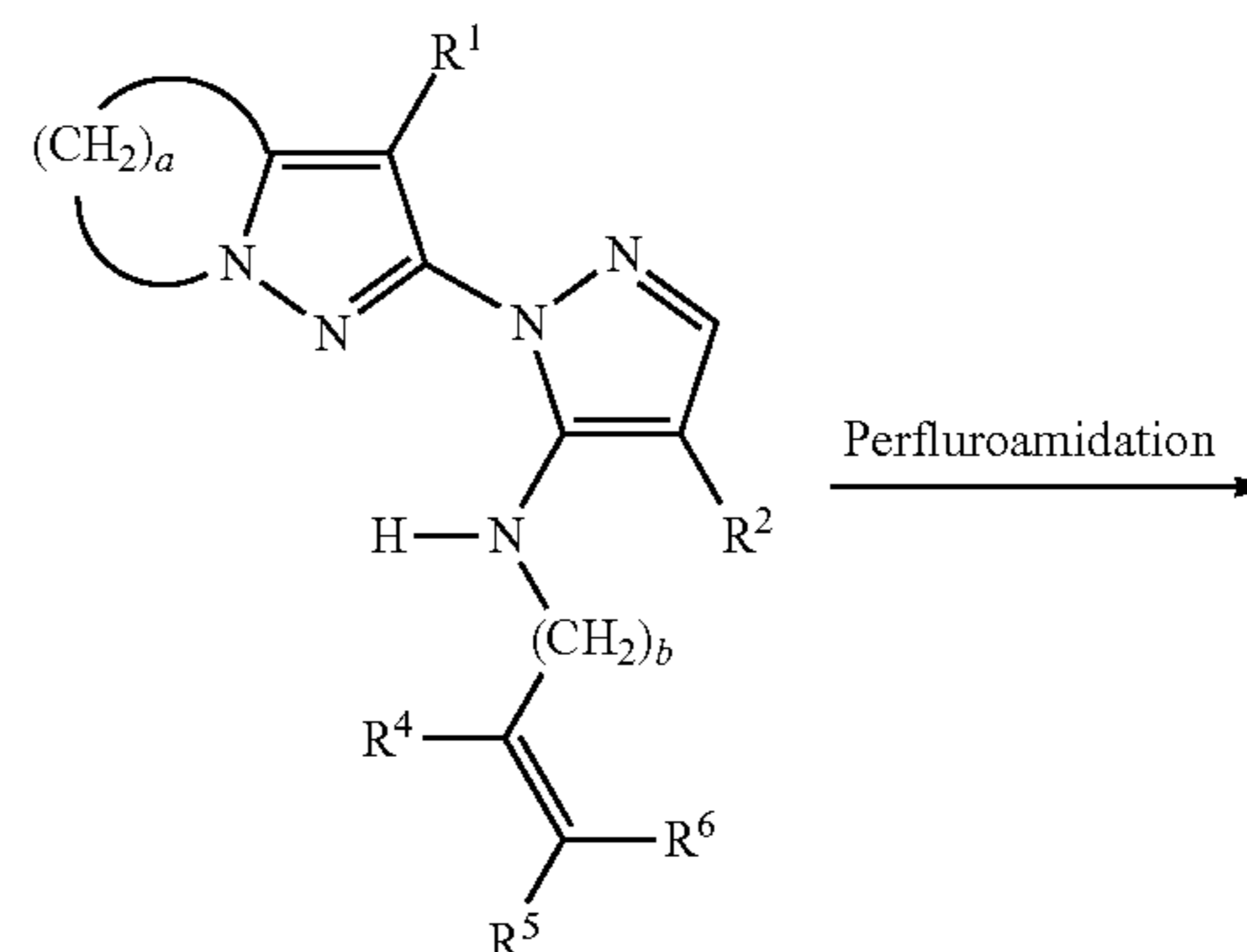
[Chemical formula 2]



(II)

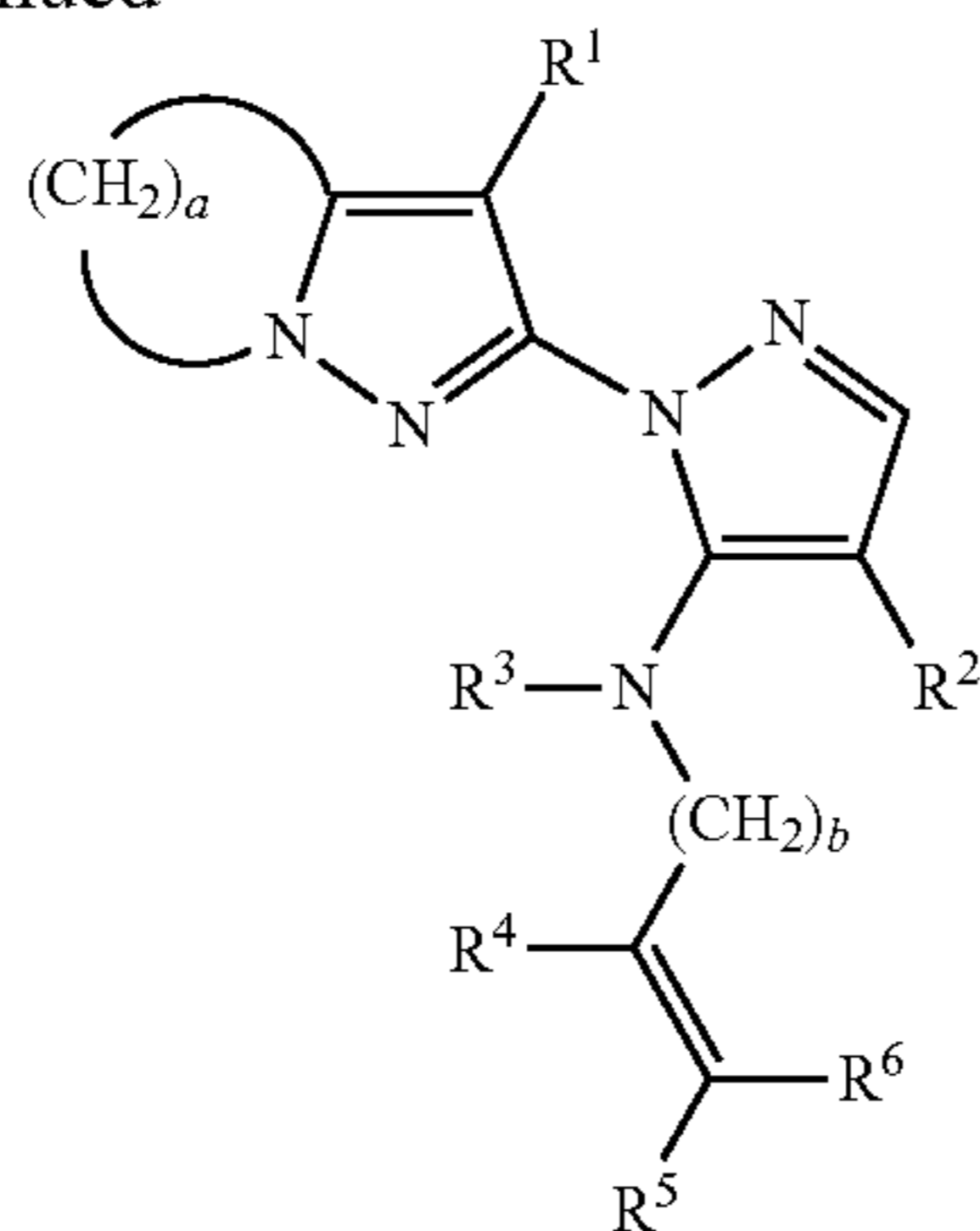
Compounds in which R³ does not contain a hydrogen atom can be synthesized by a perfluoroamidation reaction represented by the following formula (III).

[Chemical formula 3]



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-continued



(III)

The compound of formula (II) can be synthesized from tetrahydro-2H-pyran-2-ylideneacetonitrile or 5-chlorovaleryl chloride in accordance with the methods described in WO 93/10100 and WO 94/08999.

The compound represented by formula (II) can be synthesized by an alkylation reaction per se with reference to known reaction conditions (see, for example, WO 94/08999). This may also be carried out by a procedure consisting of protection of the amino group followed by alkylation and deprotection depending on the case.

The perfluoroamidation reaction per se of formula (III) can be easily carried out under known reaction conditions and a known method described in the literature cited therein (for example, Japanese Patent Application Laid-open No. 2005-154420).

The compound of formula (I) provided by the present invention has superior herbicidal efficacy and is useful as a herbicide as is clear from the results of the herbicidal activity tests described in Test Examples 1 to 3 to be subsequently described.

The compound of formula (I) of the present invention has activity against numerous types of crop weeds and non-crop weeds. Examples of cultivated plants include gramineous plants such as rice, wheat, barley, corn, oats or sorghum, broadleaf crops such as soybeans, cotton, beets, sunflowers or rapeseed, fruit trees, vegetables such as fruit vegetables, root vegetables or leafy vegetables, and grasses, and the compound of formula (I) can be used for the cultivation thereof.

The compound of the present invention has herbicidal efficacy against the various weeds listed below that cause problems in rice paddies in any of the treatment methods of soil treatment in an irrigated or unirrigated state, soil incorporation treatment and foliar treatment. Although the following lists examples thereof, these weeds are not limited to the following examples.

Examples of paddy weeds that can be controlled by the compound of formula (I) of the present invention include Alismataceous weeds such as *Alisma canaliculatum*, *Sagittaria trifolia* or *Sagittaria pygmaea*, Cyperaceous weeds such as *Cyperus difformis*, *Cyperus serotinus*, *Scirpus juncooides*, *Eleocharis kuroguwai*, *Scirpus planiculmis* or *Scirpus nipponicus*, Scrophulariaceous weeds such as *Lindernia procumbens*, *Lindernia dubia* subsp. *dubia* or *Lindernia dubia*, Pontederiaceous weeds such as *Monochoria vaginalis* or *Monochoria korsakowii*, Potamogetonaceous weeds such as *Potamogeton distinctus*, Lythraceous weeds such as *Rotala indica* or *Ammannia multiflora*, Asteraceous weeds such as *Bidens tripartita* or *Bidens frondosa*, Legumino-

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seous weeds such as *Aeschynomene indica*, Commelinaceous weeds such as *Murdannia keisak*, and Gramineous weeds such as *Echinochloa oryzicola*, *Echinochloa crus-galli* var. *crus-galli*, *Echinochloa crus-galli* var. *formosensis*, *Echinochloa crus-galli* var. *praticola*, *Echinochloa crus-galli* var. *caudata*, *Leptochloa chinensis*, *Leersia japonica*, *Paspalum distichum* or *Leersia oryzoides*.

In addition, the compound of the present invention has herbicidal efficacy against the various weeds listed below that cause problems in field land and non-crop land in any of the treatment methods of soil treatment, soil incorporation treatment and foliar treatment. Although the following lists examples thereof, these weeds are not limited to the following examples.

Examples thereof include broadleaf weeds, including Solanaceous weeds such as *Solanum nigrum* or *Datura stramonium*, Malvaceous weeds such as *Abutilon avicennae* or *Sida spinosa*, Convolvulaceous weeds such as *Ipomoea purpurea*, Amaranthaceous weeds such as *Amaranthus lividus*, Asteraceous weeds such as *Xanthium strumarium*, *Ambrosia artemisiifolia*, *Galinsoga ciliata*, *Cirsium arvense*, *Senecio vulgaris* or *Stenactis annuus*, Brassicaceous weeds such as *Rorippa indica*, *Sinapis arvensis* or *Capsella bursa-pastoris*, Polygonaceous weeds such as *Persicaria longiseta* or *Fallopia convolvulus*, Portulacaceous weeds such as *Portulaca oleracea*, Chenopodiaceous weeds such as *Chenopodium album*, *Chenopodium ficifolium* or *Kochia scoparia*, Caryophyllaceous weeds such as *Stellaria media*, Scrophulariaceous weeds such as *Veronica persica*, Commelinaceous weeds such as *Commelina communis*, Lamiaceous weeds such as *Lamium amplexicaule* or *Lamium purpureum*, Euphorbiaceous weeds such as *Euphorbia supina* or *Euphorbia maculata*, Rubiaceous weeds such as *Galium spurium*, *Galium spurium* var. *Echinosperrmon* or *Rubia argyi*, Violaceous weeds such as *Viola mandshurica*, and Leguminoseous weeds such as *Sesbania exaltata* or *Cassia obfusitolia*, and Gramineous weeds such as *Sorghum bicolor*, *Panicum dichotomiflorum*, *Sorghum halepense*, *Echinochloa crus-galli* var. *crus-galli*, *Digitaria ciliaris*, *Avena fatua*, *Eleusine indica*, *Setaria viridis*, *Alopecurus aequalis* or *Poa annua*, and Cyperaceous weeds such as *Cyperus rotundus*.

Moreover, the compound of the present invention is also able to control a wide range of weeds growing in mowed swaths, fallow land, orchards, grasslands, lawn grass plots, train line caps, vacant land and forest land, or on farm roads, causeways and other non-crop land.

Moreover, the compound of formula (I) of the present invention does not demonstrate phytotoxicity that becomes a problem for paddy rice in the case of any cultivation method such as direct seeding cultivation or transplantation cultivation of paddy rice.

The compound of formula (I) of the present invention can be applied before or after plant germination and can be mixed into soil before seeding.

Although the dosage of the compound of formula (I) of the present invention can be varied over a wide range corresponding to the type of compound, type of target plant, application window, location of application, properties of desired effects and the like, and as a general reference thereof, the dosage can be within the range of about 0.01 g to 100 g, and preferably about 0.1 g to 10 g, as the amount of active compound per are.

Although the compound of formula (I) of the present invention can be used alone, a formulation assistant and the like is normally incorporated in the compound of formula (I) in accordance with ordinary methods, and although there are

no limitations thereon, it is preferably formulated and used in any arbitrary drug form such as a dustable powder, emulsifiable concentrate, oil miscible liquid, solubilizing agent, suspo-emulsion, fine granule, aerosol spray, less drifting dust, micro granule fine, fine grains F, granules, wettable powder, water dispersible granules, flowable concentrate, throw-in types (Jumbo), tablets, paste, emulsion in oil, water soluble powder, water soluble granule, soluble concentration or capsule suspension.

There are no limitations on formulation assistants able to be used for formulation, and examples include solid vehicles, liquid vehicles, binders, thickeners, surfactants, anti-freezing agents and preservatives.

Examples of solid vehicles include, but are not limited to, talc, bentonite, montmorillonite, clay, kaolin, calcium carbonate, sodium carbonate, sodium bicarbonate, mirabilite, zeolite, starch, acidic clay, diatomaceous earth, chaoite, vermiculite, slaked lime, vegetable powder, alumina, activated carbon, sugars, hollow glass, silica sand, ammonium sulfate and urea.

Examples of liquid vehicles include, but are not limited to, hydrocarbons (such as kerosene or mineral oil), aromatic hydrocarbons (such as toluene, xylene, dimethyl naphthalene or phenyl xylyl ethane), chlorinated hydrocarbons (such as chloroform or carbon tetrachloride), ethers (such as dioxane or tetrahydrofuran), ketones (such as acetone, cyclohexanone or isophorone), esters (such as ethyl acetate, ethylene glycol acetate or dibutyl maleate), alcohols (such as methanol, n-hexanol or ethylene glycol), polar solvents (such as N,N-dimethylformamide, dimethylsulfoxide or N-methylpyrrolidone) and water.

Examples of binders and thickeners include, but are not limited to, dextrin, sodium salts of carboxymethyl cellulose, polycarboxylic acid-based polymer compounds, polyvinylpyrrolidone, polyvinyl alcohol, sodium lignin sulfonate, calcium lignin sulfonate, sodium polyacrylate, gum arabic, sodium alginate, mannitol, sorbitol, bentonite-based mineral matter, polyacrylic acid and derivatives thereof, chaoite and natural sugar derivatives (such as xanthan gum or guar gum).

Examples of surfactants include, but are not limited to, anionic surfactants such as fatty acid salts, benzoates, alkyl-sulfosuccinates, dialkylsulfosuccinates, polycarboxylates, alkyl sulfate ester salts, alkyl sulfates, alkyl aryl sulfates, alkyl diglycol ether sulfates, alcohol sulfate ester salts, alkyl sulfonates, alkyl aryl sulfonates, aryl sulfonates, lignin sulfonates, alkyl diphenyl ether disulfonates, polystyrene sulfonates, alkyl phosphate ester salts, alkyl aryl phosphates, styryl aryl phosphates, polyoxyethylene alkyl ether sulfate ester salts, polyoxyethylene alkyl aryl ether sulfates, polyoxyethylene alkyl aryl ether sulfate ester salts, polyoxyethylene alkyl ether phosphates, polyoxyethylene alkyl aryl phosphate ester salts or salts of naphthalene sulfonate-formalin condensates, and nonionic surfactants such as sorbitan fatty acid esters, glycerin fatty acid esters, fatty acid polyglycerides, fatty acid alcohol polyglycol ethers, acetylene glycol, acetylene alcohol, oxyalkylene block polymers, polyoxyethylene alkyl ethers, polyoxyethylene alkyl aryl ethers, polyoxyethylene styryl aryl ethers, polyoxyethylene glycol alkyl ethers, polyoxyethylene fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene glycerin fatty acid esters, polyoxyethylene hydrogenated castor oil or polyoxypropylene fatty acid esters.

Examples of anti-freezing agents include, but are not limited to, ethylene glycol, diethylene glycol, propylene glycol and glycerin.

Examples of preservatives include, but are not limited to, benzoic acid, sodium benzoate, methyl paraoxybenzoate, butyl paraoxybenzoate, isopropyl methyl phenol, benzalkonium chloride, chlorhexidine hydrochloride, aqueous hydrogen peroxide, chlorhexidine gluconate, salicylic acid, sodium salicylate, zinc pyrithione, sorbic acid, potassium sorbate, dehydroacetic acid, sodium dehydroacetate, phenoxyethanol, isothiazoline derivatives such as 5-chloro-2-methyl-4-isothiazolin-3-one or 2-methyl-4-isothiazolin-3-one, 2-bromo-2-nitropropane-1,3-diol and salicylic acid derivatives.

The previously mentioned solid vehicles, liquid vehicles, binders, thickeners, surfactants, anti-freezing agents and preservatives can each be used alone or in a suitable combination thereof corresponding to the purpose of use and the like.

Although the incorporated ratio of the compound of formula (I) of the present invention with respect to the total herbicide composition of the present invention can be increased or decreased as necessary and there are no particular limitations thereon, it is normally about 0.01% by weight to 90% by weight, and for example, in the case of being in the form of a dustable powder or granules, is preferably about 0.1% by weight to 50% by weight and more preferably about 0.5% by weight to 10% by weight, while in the case of being in the form of an emulsifiable concentrate, wettable powder or water dispersible granules, is preferably about 0.1% by weight to 90% by weight and more preferably about 0.5% by weight to 50% by weight.

These preparations can be provided for use in various types of applications by diluting to a suitable concentration as necessary followed by spraying or applying directly to plant foliage, soil or the surface of a rice paddy and the like.

The following provides an explanation of the present invention through examples thereof.

EXAMPLES

Example 1

Method for the Synthesis of 1-(3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridin-2-yl)-5-(2-methylprop-2-enylamino)pyrazole-4-carbonitrile (Compound 1)

Acetonitrile (75 ml) was added to 5-amino-1-(3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridin-2-yl)pyrazole-4-carbonitrile (19.7 g) followed by slowly dropping acetyl chloride (5.8 g) therein and refluxing for 5 hours. Following completion of the reaction, water was added to the reaction mixture and the precipitated solid was washed with ethyl acetate to obtain N-(1-(3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridin-2-yl)-4-cyanopyrazol-5-yl)acetamide (12 g).

N-(1-(3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridin-2-yl)-4-cyanopyrazol-5-yl)acetamide (2.5 g) was dissolved in acetonitrile (8 ml) followed by the addition of potassium carbonate (1.3 g) and stirring. 3-chloro-2-methyl-1-propene (0.8 g) was then added thereto followed by refluxing for 8 hours. Following completion of the reaction, water was added to the reaction mixture followed by extraction with ethyl acetate. After drying with sodium sulfate, the solvent was concentrated under reduced pressure and the resulting solid was purified by silica gel column chromatography (hexane/ethyl acetate=1:1). The purified compound (1.3 g) was dissolved in ethanol (3 ml) followed by the addition of sodium hydroxide (0.14 g) and water (1 ml) and reacting for 1 day at room temperature. Following completion of the

reaction, water was added to the reaction liquid and the precipitated solid was washed with isopropyl ether to obtain the desired compound (0.8 g).

Example 2

Method for the Synthesis of 1-(3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridin-2-yl)-5-(2-chloroprop-2-enylamino)pyrazole-4-carbonitrile (Compound 2)

Formic acid (18.4 g) was slowly dropped into acetic anhydride (33.7 g) cooled to 5° C. followed by stirring for 2 hours at 60° C. (Reaction Mixture A). Separate from the above, 5-amino-1-(3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridin-2-yl)pyrazole-4-carbonitrile (26.3 g) was dissolved in acetonitrile (200 ml) and stirred. The previously prepared Reaction Mixture A was slowly dropped therein and reacted for 1 day at room temperature and then for 4 hours at 60° C. Subsequently, the solvent was concentrated under reduced pressure followed by neutralizing using aqueous potassium carbonate solution, washing the precipitated solid with water and drying to obtain N-(1-(3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridin-2-yl)-4-cyanopyrazol-5-yl)formamide (28 g).

N-(1-(3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridin-2-yl)-4-cyanopyrazol-5-yl)formamide (1.5 g) was dissolved in acetonitrile (5 ml) followed by adding potassium carbonate (0.8 g) and stirring. 2,3-dichloro-1-propene (0.6 g) was slowly dropped therein and reacted for 3 hours at 40° C., and following completion of the reaction, water was added to the reaction mixture followed by extraction with ethyl acetate. After drying with sodium sulfate, the solvent was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (hexane/ethyl acetate=1:1) to obtain N-(1-(3-chloro-4,5,6,7-tetrahydropy-

razolo[1,5-a]pyridin-2-yl)-4-cyanopyrazol-5-yl)-N-(2-chloroprop-2-enyl)formamide (1.73 g).

N-(1-(3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridin-2-yl)-4-cyanopyrazol-5-yl)-N-(2-chloroprop-2-enyl)formamide (1.73 g) was dissolved in ethanol (5 ml) followed by the addition of 10% hydrochloric acid (6.9 g) and stirring for 3 hours at room temperature. Following completion of the reaction, water was added to the reaction mixture and the precipitated solid was filtered out and dried to obtain the desired compound (4.1 g).

Example 3

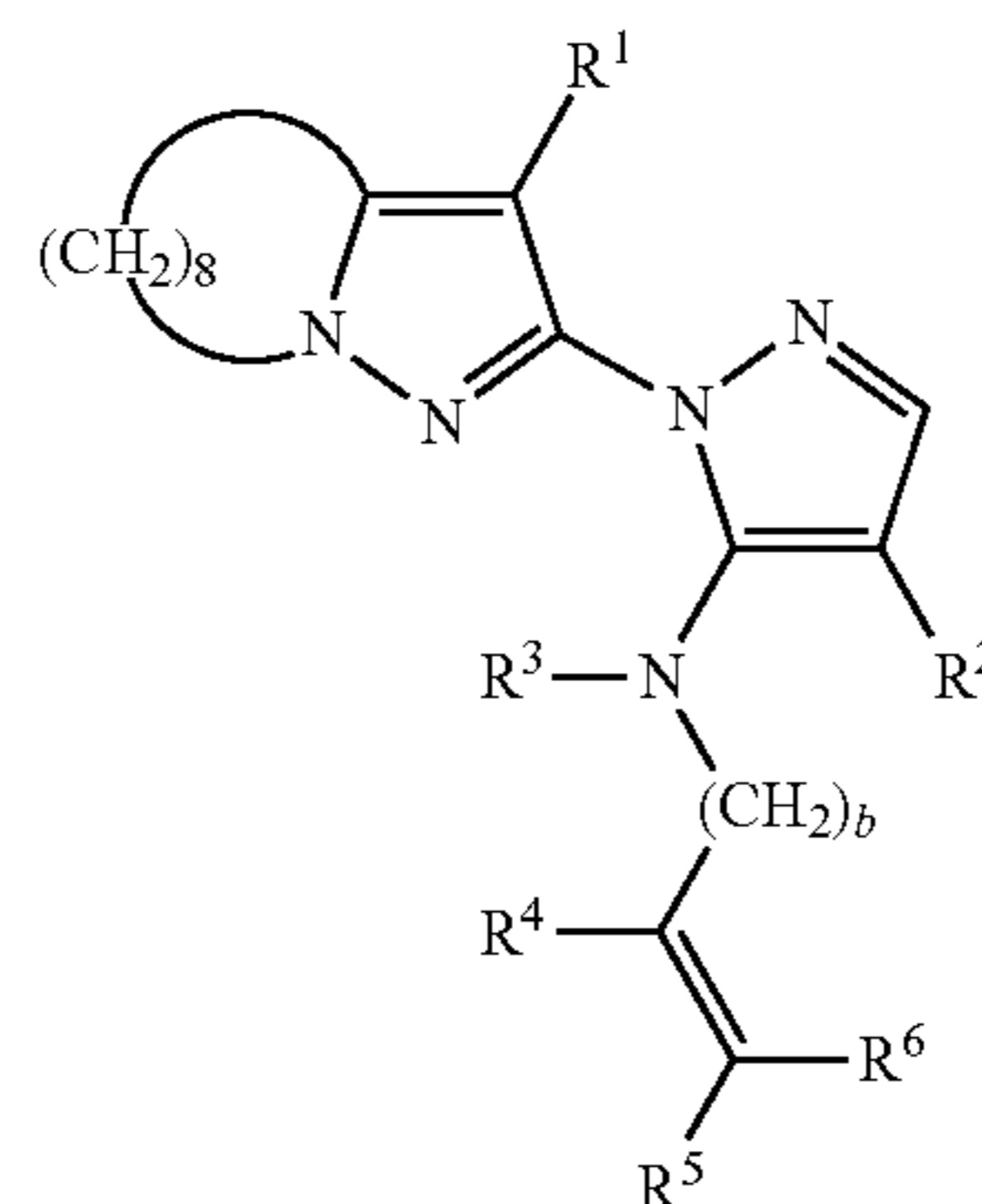
Method for the Synthesis of (N-1-(3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridin-2-yl)-4-cyanopyrazol-5-yl)-N-(2-chloroprop-2-enyl)-2,2,2-trifluoroacetamide (Compound 3)

1-(3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridin-2-yl)-5-(2-chloroprop-2-enyl)pyrazole-4-carbonitrile (0.7 g) was dissolved in acetonitrile (5 ml) followed by slowly dropping in trifluoroacetic anhydride (1.3 g). After stirring for 7 days at 40° C., saturated aqueous sodium hydrogen carbonate solution was added to the reaction liquid followed by extracting with ethyl acetate. After drying with sodium sulfate, the solvent was distilled off under reduced pressure and the resulting crude product was purified by silica gel column chromatography (hexane/ethyl acetate=4:1) to obtain the desired compound (0.4 g).

The starting material in the form of the compound of formula (II) was synthesized in accordance with WO 93/10100 and WO 94/08999.

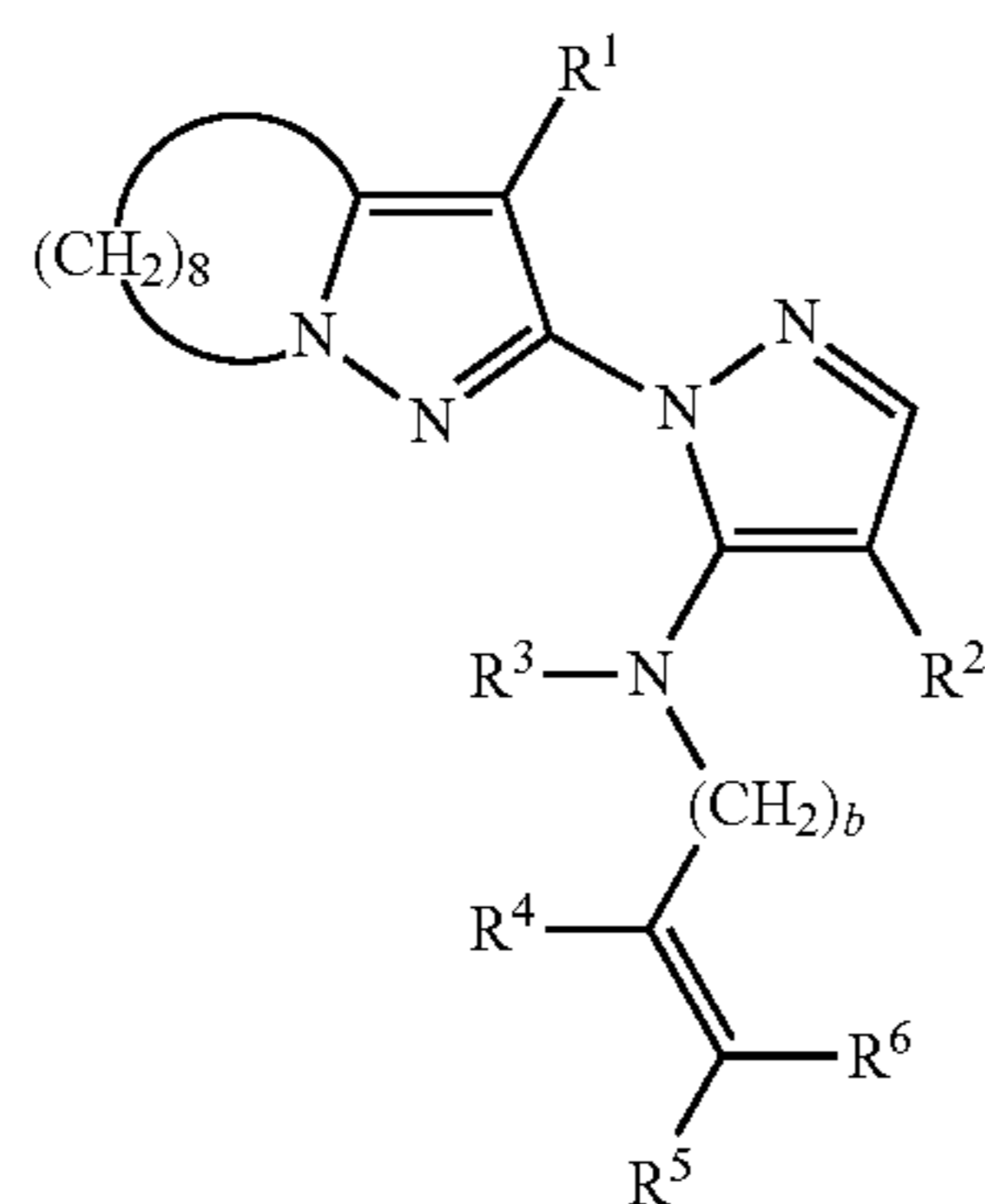
The examples listed in the following tables can be synthesized by the same manner as the above-mentioned methods or obtained in the same manner as the above-mentioned methods.

TABLE 1



Compound	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	cis/trans	a	b	mp	Refractive index (° C.)
1	Cl	CN	H	CH ₃	H	H		4	1	97-98	
2	Cl	CN	H	Cl	H	H		4	1	123-124	
3	Cl	CN	COCF ₃	Cl	H	H		4	1	95-96	
4	Cl	CN	H	H	Ph	H	trans	4	1	127-128	
5	Cl	CN	H	H	H	H		4	2	130-131	
6	Cl	CN	H	F	F	F		4	2	111-112	
7	Cl	CN	H	H	Cl	H	cis	4	1	126	
8	Cl	CN	H	H	Cl	H	trans	3	1		
9	Cl	CN	H	H	Cl	H	cis	3	1		
10	Cl	CN	H	H	Cl	H	trans	4	1		
11	Cl	CN	H	Cl	Cl	H	mix	4	1	125-126	
12	Cl	CN	H	H	CH ₃	H	mix	4	1	114-115	
13	Cl	CN	H	H	CH ₃	CH ₃		4	1	75-76	
14	Cl	CN	H	H	CH ₃	H	mix	4	2		

TABLE 1-continued



Compound	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	cis/trans	a	b	mp	Refractive index (° C.)
15	Cl	CN	H	H	CH ₃	H	mix	3	1		
16	Cl	CN	COCF ₃	H	Ph	H	mix	4	1	100	
17	Cl	CN	COCF ₃	H	H	H		4	1	91-92	
18	Cl	CN	COCF ₃	H	H	H		4	2		1.5270(22.9)
19	Cl	CN	COCF ₃	CH ₃	H	H		4	1	85-86	
20	Cl	CN	COCF ₃	F	F	F		4	2		
21	Cl	CN	COCF ₃	H	Cl	H	cis	4	1	90-91	
22	Cl	CN	COCF ₃	H	Cl	H	trans	4	1		
23	Cl	CN	COCF ₃	Cl	Cl	H	mix	4	1	99-100	
24	Cl	CN	COCF ₃	H	CH ₃	H	mix	4	1	108-109	
25	Cl	CN	COCF ₃	H	CH ₃	CH ₃		4	1	67-68	
26	Cl	CN	COCF ₃	H	CH ₃	H	mix	4	2		
27	Cl	CN	COCF ₃	H	CH ₃	H	mix	3	1		
28	Cl	CN	COC ₂ F ₅	H	H	H		4	1		1.5074(28.1)
29	Cl	NO ₂	H	H	H	H		4	2		
30	Cl	NO ₂	H	Cl	H	H		4	1	150	
31	Cl	NO ₂	H	CH ₃	H	H		4	1	91-92	
32	Cl	NO ₂	H	H	Cl	H	cis	4	1	147-148	
33	Cl	NO ₂	H	Cl	Cl	H	mix	4	1	154-156	
34	Cl	NO ₂	H	H	CH ₃	H	mix	4	1	102-103	
35	Cl	NO ₂	H	H	CH ₃	CH ₃		4	1	82-83	
36	Cl	NO ₂	COCF ₃	H	H	H		4	1	85	
37	Cl	NO ₂	COCF ₃	H	H	H		4	2	66-67	
38	Cl	NO ₂	COCF ₃	CH ₃	H	H		4	1	116-117	
39	Cl	NO ₂	COCF ₃	H	Cl	H	cis	4	1	80	
40	Cl	NO ₂	COCF ₃	H	CH ₃	H	mix	4	1	102-103	
41	Cl	NO ₂	COCF ₃	H	CH ₃	CH ₃		4	1	72-73	
42	Br	CN	H	H	H	H		4	2	129-130	
43	Br	CN	H	Cl	H	H		4	1	129-130	
44	Br	CN	H	CH ₃	H	H		4	1	105-106	
45	Br	CN	H	H	Cl	H	cis	4	1	105-106	
46	Br	CN	H	Cl	Cl	H	mix	4	1	137-138	
47	Br	CN	H	H	CH ₃	H	mix	4	1	120-121	
48	Br	CN	H	H	CH ₃	CH ₃		4	1	83-84	
49	Br	CN	COCF ₃	H	H	H		4	1	107-108	
50	Br	CN	COCF ₃	H	H	H		4	2	70-71	
51	Br	CN	COCF ₃	Cl	H	H		4	1	107-108	
52	Br	CN	COCF ₃	CH ₃	H	H		4	1	85	
53	Br	CN	COCF ₃	H	Cl	H	cis	4	1	102-103	
54	Br	CN	COCF ₃	Cl	Cl	H		4	1		1.5480(25.0)
55	Br	CN	COCF ₃	H	CH ₃	H	mix	4	1	70-71	
56	Br	CN	COCF ₃	H	CH ₃	CH ₃		4	1		1.5308(26.4)
57	Br	NO ₂	H	H	CH ₃	H	mix	4	1	105-106	
58	Br	NO ₂	COCF ₃	H	H	H		4	1	99	
59	Br	NO ₂	COCF ₃	H	CH ₃	H	mix	4	1	103-104	

Preparation Examples

A dustable powder is obtained by mixing the above components and finely crushing with a hammer mill.

1. Dustable Powder

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2. Wettable Powder

Compound of formula (I)	10 parts by weight
Talc	90 parts by weight

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Compound of formula (I)	10 parts by weight
Polyoxyethylene alkyl aryl ether sulfate	22.5 parts by weight
White carbon	67.5 parts by weight

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A wettable powder is obtained by mixing the above components and finely crushing the mixture with a hammer mill.

3. FLOWABLE CONCENTRATE

Compound of formula (I)	10 parts by weight
Polyoxyethylene alkyl ether phosphate	10 parts by weight
Bentonite	5 parts by weight
Ethylene glycol	5 parts by weight
Water	70 parts by weight

A flowable concentrate is obtained by mixing the above components and crushing using a wet pulverizer.

4. Emulsifiable Concentrate

Compound of formula (I)	15 parts by weight
Ethoxylated nonylphenol	10 parts by weight
Cyclohexanone	75 parts by weight

An emulsifiable concentrate is obtained by mixing the above components.

5. Granules

Compound of formula (I)	5 parts by weight
Calcium lignin sulfonate	3 parts by weight
Polycarboxylate	3 parts by weight
Calcium carbonate	89 parts by weight

The above components are mixed followed by adding water, kneading, extruding and granulating. Subsequently, granules are obtained by drying followed by sizing.

Biological Testing Examples

1. Paddy Herbicidal Activity Test

Rice paddy soil was filled into a $\frac{1}{10000}$ are pot followed by the addition of suitable amounts of water and chemical fertilizer, kneading, seeding with *Echinochloa crus-galli*, *Monochoria vaginalis* and *Scirpus juncooides* and maintaining in an irrigated state at a water depth of 3 cm.

Wettable powder of Target Compound (I) shown in Table 1 prepared in compliance with the preparation examples were diluted with a suitable amount of water, rice plants in the 2.0 leaf stage were transplanted during 3.5 leaf stage of *Echinochloa crus-galli*, and treated by dropping in chemical in the prescribed amount per are using a pipette.

After treating for 30 days in a glass greenhouse at an average atmospheric temperature of 30° C., the herbicidal efficacy thereof was investigated.

Evaluation of herbicidal efficacy was carried out by comparing growth inhibition rate (%) with an untreated group, while evaluation of phytotoxicity was carried out by comparing growth inhibition rate (%) with the state of a complete eradication group, and were evaluated at 11 levels indicated below.

- 0 (exponent): 0% to less than 10% (growth inhibition rate)
 1: 10% to less than 20%
 2: 20% to less than 30%

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3: 30% to less than 40%

4: 40% to less than 50%

5: 50% to less than 60%

6: 60% to less than 70%

7: 70% to less than 80%

8: 80% to less than 90%

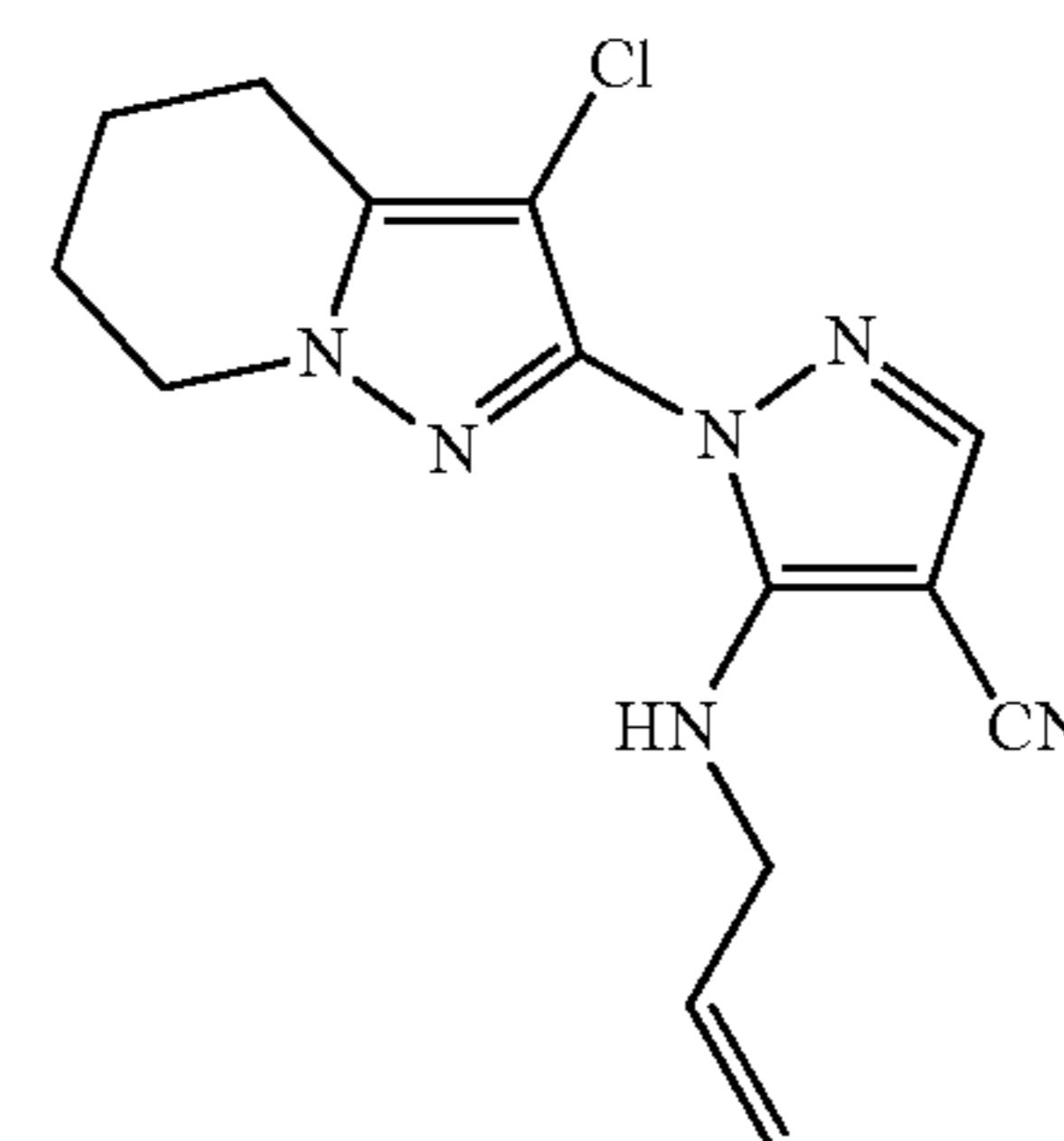
9: 90% to less than 100%

10: 100%

The results are shown in Table 2.

Control agent 4.59 (described in WO 94/08999)

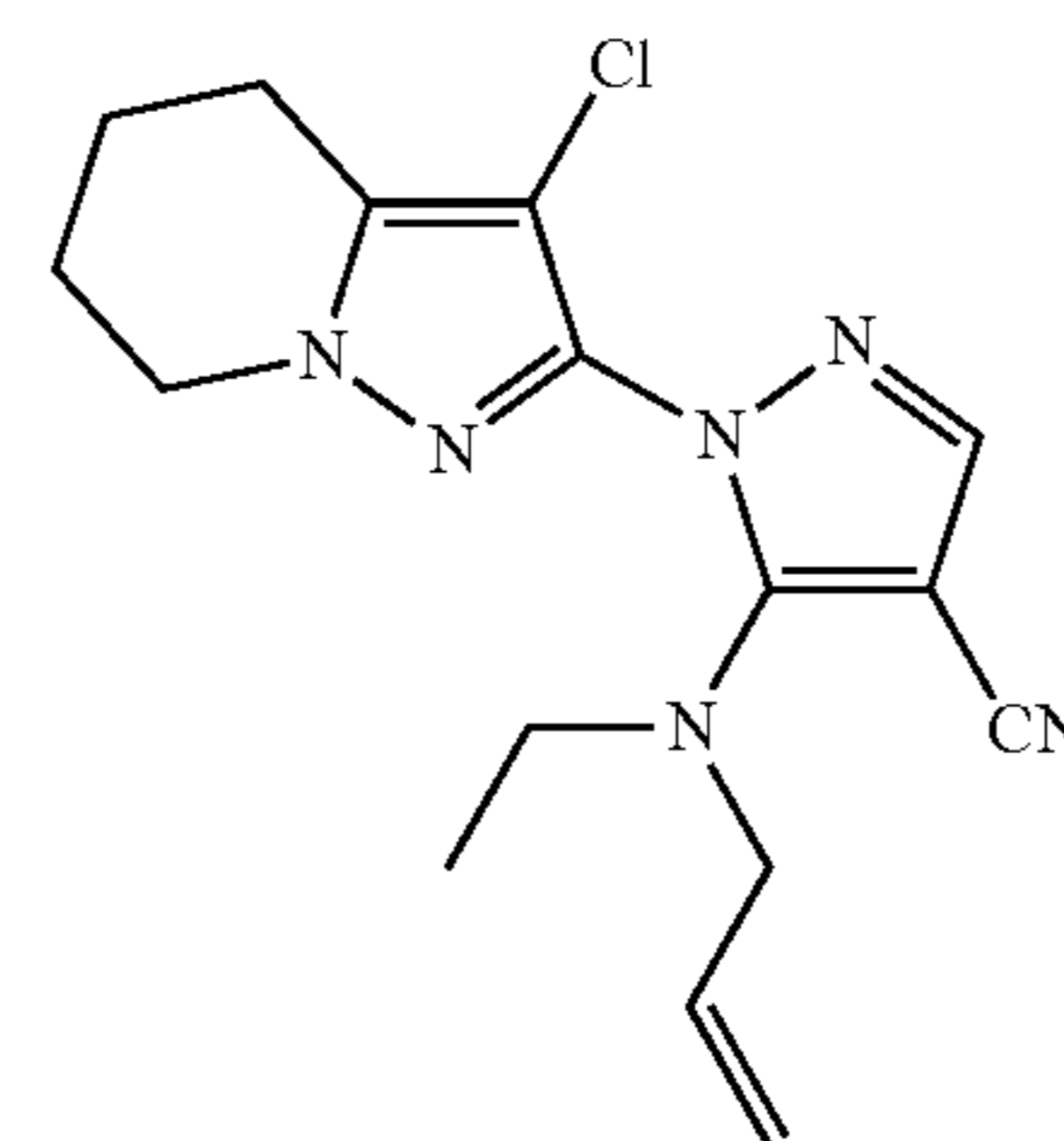
[Chemical formula 4]



(4.59)

Control agent 4.75 (described in WO 94/08999)

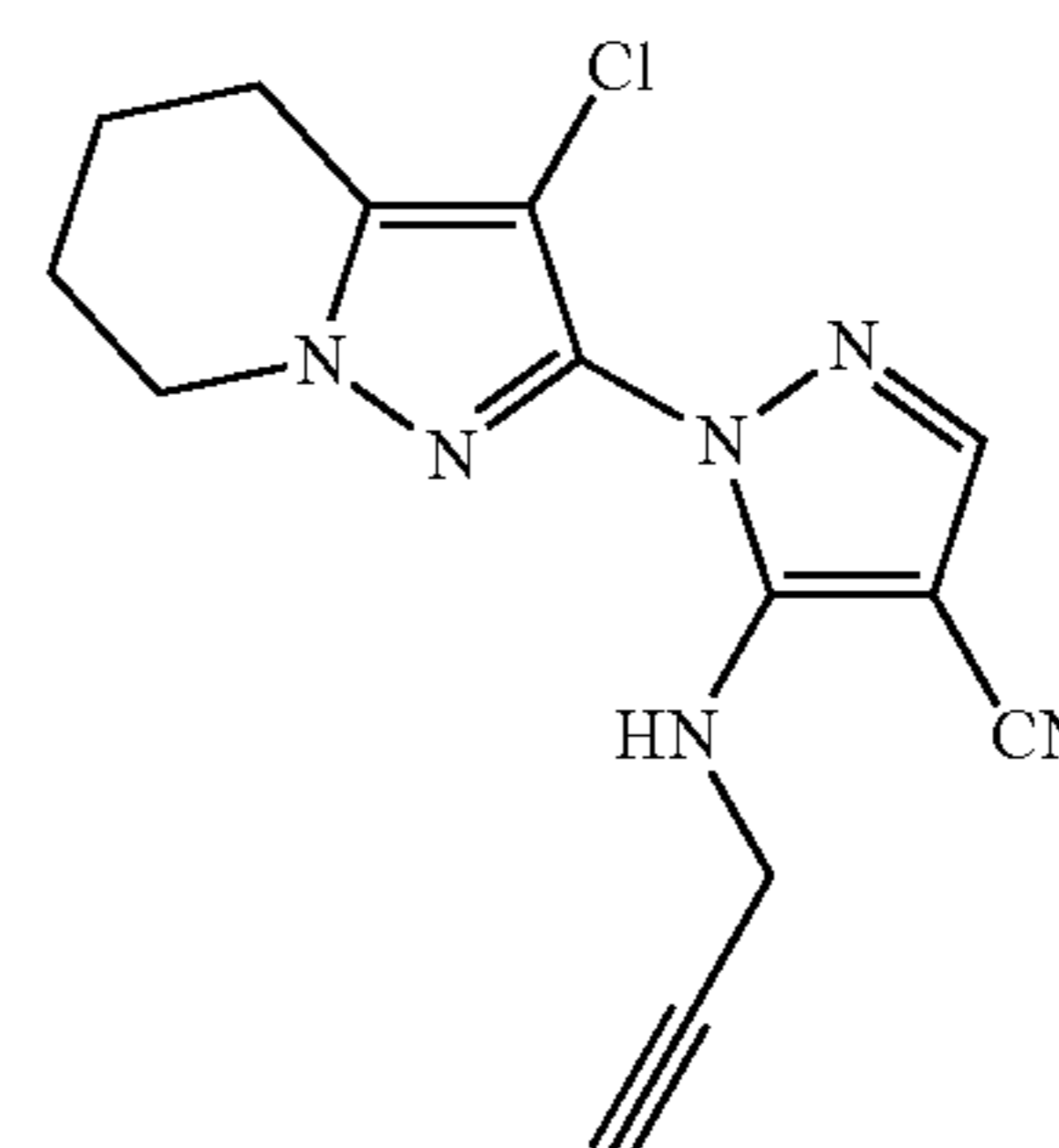
[Chemical formula 5]



(4.75)

Control agent 4.85, 4.156 (described in WO 94/08999)

[Chemical formula 6]



(4.85, 4.156)

Control agent 4.239 (described in WO 94/08999)

[Chemical formula 7]

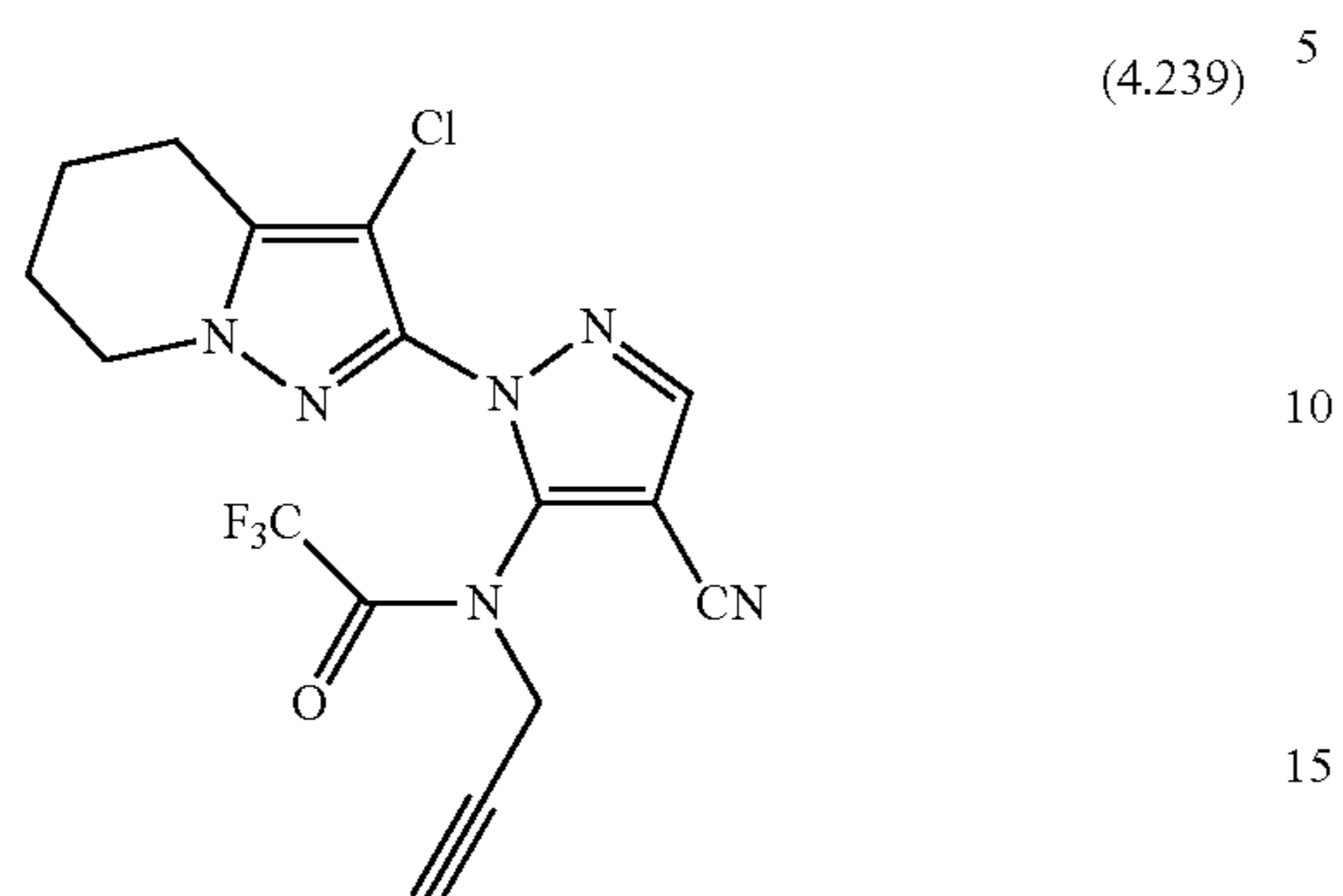


TABLE 2

Compound	5g ^{a.i.} /10a				1g ^{a.i.} /10a			
	<i>Echinochloa crus-galli</i>	<i>Scirpus juncooides</i>	<i>Monochoria vaginalis</i>	Rice plants	<i>Echinochloa crus-galli</i>	<i>Scirpus juncooides</i>	<i>Monochoria vaginalis</i>	Rice plants
1	9	8	9	0	8	7	9	0
2	9	8	9	0	9	7	9	0
3	10	8	9	0	9	7	9	0
5	10	8	9	1	9	7	9	0
6	9	8	8	1	9	8	7	0
7	9	8	9	0	9	7	9	0
11	9	8	9	0	8	7	8	0
12	10	9	10	1	9	8	9	0
13	10	8	9	1	9	8	8	0
17	10	9	8	1	9	9	8	0
18	9	8	9	1	9	7	8	0
19	10	8	9	0	9	7	9	0
20	9	8	9	0	9	8	8	0
21	9	10	9	0	9	8	9	0
23	9	8	9	0	8	7	8	0
24	10	9	9	1	9	8	8	0
25	10	8	9	1	9	8	9	0
26	9	8	9	0	9	7	8	0
28	9	9	10	0	9	8	8	0
30	10	10	10	0	9	8	9	0
31	9	8	9	0	9	7	9	0
32	9	10	10	1	8	8	9	0
34	9	8	9	0	9	8	9	0
35	9	10	10	1	9	8	9	0
36	10	9	9	1	9	8	8	0
39	10	8	8	1	9	8	7	0
40	9	8	8	0	8	7	8	0
42	9	8	8	0	8	8	7	0
45	9	9	9	1	9	9	9	1
46	8	8	8	1	7	7	7	0
47	10	8	9	0	9	7	8	0
48	9	8	10	1	8	7	8	1
49	9	9	9	1	8	8	7	1
50	10	8	9	1	9	7	7	0
51	9	8	8	0	9	8	8	0
53	10	8	8	1	9	7	7	1
57	10	8	9	0	9	7	8	0
4.59	5	4	4	2	2	2	2	1
4.75	4	2	5	1	3	2	4	0
4.85, 4.156	3	1	3	2	2	0	1	2
4.239	5	1	2	1	3	0	1	0

2. Farming Soil Treatment Test

Field soil was filled into a 1/6000 are pot followed by seeding with *Digitaria ciliaris*, *Chenopodium album* and *Amaranthus retroflexus* and covering with soil.

Wettable powder of compounds of formula (I) shown in Table 1 prepared in compliance with the preparation examples were diluted with water to the prescribed amount

of chemical and uniformly sprayed onto each soil surface layer using 10 liters of sprayed water per are prior to weed growth following seeding.

After treating for 30 days in a glass greenhouse at an average atmospheric temperature of 30° C., the herbicidal efficacy thereof was investigated.

Evaluation of herbicidal efficacy is carried out in the same manner as the above-mentioned Test Example 1.

The results are shown in Table 3.

TABLE 3

Compound	10g ^{a.i.} /10a			5g ^{a.i.} /10a		
	<i>Digitaria ciliaris</i>	<i>Chenopodium album</i>	<i>Amaranthus retroflexus</i>	<i>Digitaria ciliaris</i>	<i>Chenopodium album</i>	<i>Amaranthus retroflexus</i>
3	10	10	10	10	10	10
12	10	10	10	10	10	10
21	10	10	10	10	10	10
24	10	10	10	10	10	10
30	10	10	10	10	10	10
32	10	10	10	10	10	10
4.59	6	6	6	5	5	5
4.75	4	6	6	3	5	6
4.85, 4.156	4	5	6	3	4	3
4.239	5	3	5	4	2	3

3. Weed Foliar Treatment Test

Soil was filled into a 1/6000 are pot followed by seeding with *Digitaria ciliaris*, *Chenopodium album* and *Amaranthus retroflexus*, covering with soil, and cultivating in a glass greenhouse at an average atmospheric temperature of 25° C.

Wettable powder of Target Compound (I) shown in Table 1 prepared in compliance with the preparation examples were diluted with water to the prescribed amount of chemical and uniformly sprayed onto the weeds using 15 liters of sprayed water per are when *Digitaria ciliaris* had grown to the 1.0 to 2.0 leaf stage.

After treating for 3 weeks in a glass greenhouse at an average atmospheric temperature of 25° C., the herbicidal efficacy thereof was investigated.

Evaluation of herbicidal efficacy was carried out in the same manner as the above-mentioned Test Example 1.

The results are shown in Table 4.

TABLE 4

Compound	10g ^{a.i.} /10a			5g ^{a.i.} /10a		
	<i>Digitaria ciliaris</i>	<i>Chenopodium album</i>	<i>Amaranthus retroflexus</i>	<i>Digitaria ciliaris</i>	<i>Chenopodium album</i>	<i>Amaranthus retroflexus</i>
3	10	10	10	10	10	10
12	10	10	10	10	10	10
21	10	10	10	10	10	10
24	10	10	10	10	10	10
30	10	10	10	10	10	10
32	10	10	10	10	10	10
4.59	6	7	7	4	6	6
4.75	5	7	7	4	6	5
4.85, 4.156	5	6	6	3	5	4
4.239	5	4	6	3	3	4

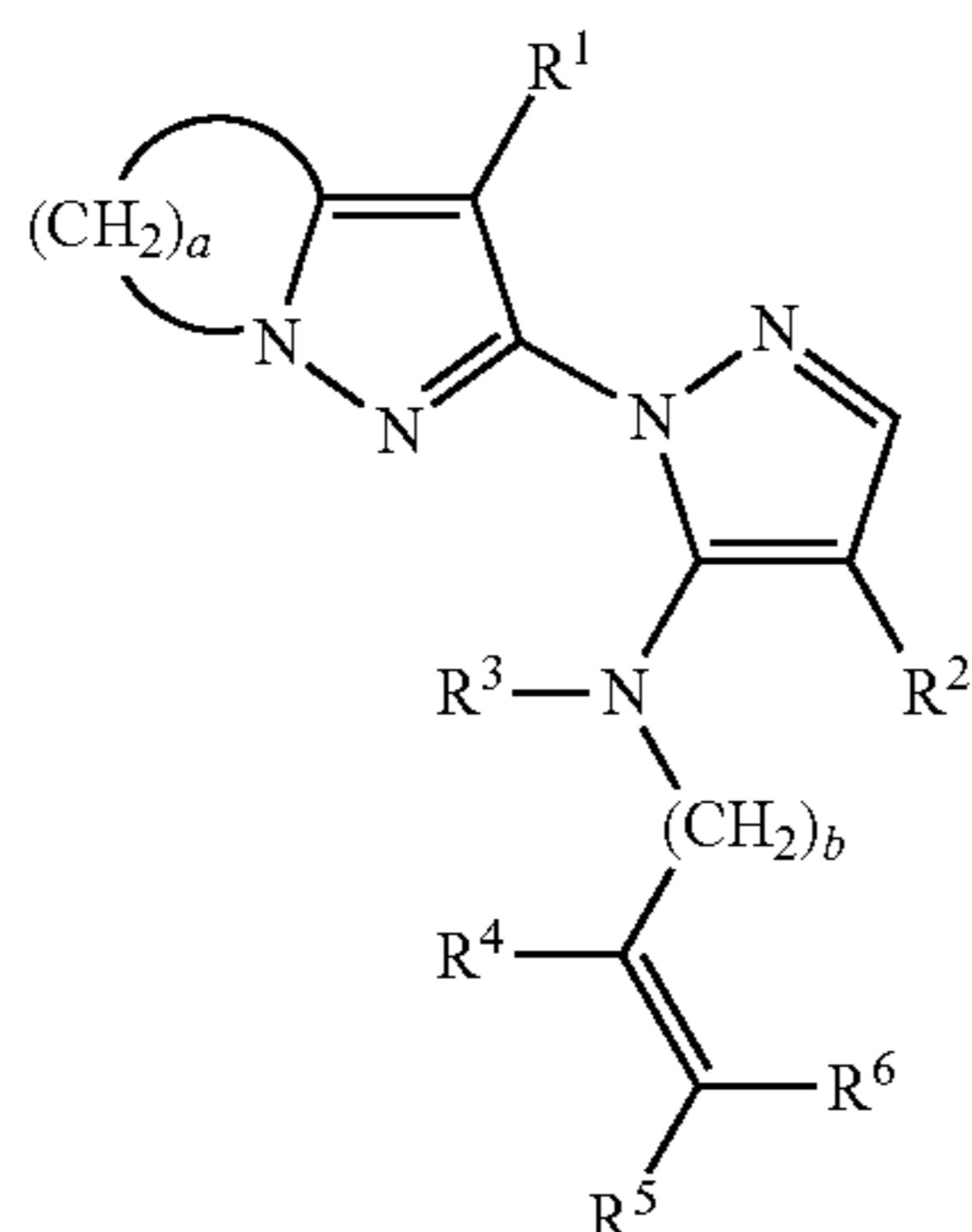
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INDUSTRIAL APPLICABILITY

According to the present invention, the compound for formula (I) of the present invention is useful as a herbicide against harmful plants since it has superior herbicidal efficacy against undesirable plants.

The invention claimed is:

1. A compound represented by the following formula (I):



wherein,

R¹ represents a halogen atom,

R² represents a cyano group or nitro group,

R³ represents a hydrogen atom, trifluoroacetyl group, pentafluoropropionyl group or heptafluorobutenyl group,

R⁴, R⁵ and R⁶ may be the same or different and represent (i) one or more hydrogen atoms, (ii) one or more halogen atoms, (iii) one or more C₁-C₆ alkyl groups optionally substituted with one or more halogen atoms, (iv) one or more C₃-C₆ cycloalkyl groups optionally substituted with one or more halogen atoms, (v) one or more C₁-C₆ alkoxy-C₁-C₆-alkyl groups optionally substituted with one or more halogen atoms or (vi) one or more phenyl groups optionally substituted with one or more halogen atoms, nitro groups, cyano groups, C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms or C₁-C₄ alkoxy groups,

a represents 3 to 5, and

b represents 0 to 2;

excluding compounds in which R¹ represents a halogen atom, R² represents a cyano group, R³, R⁴, R⁵ and R⁶ represent hydrogen atoms and b is 1.

2. The compound according to claim 1, wherein

R¹ represents a chlorine atom or bromine atom,

R⁴, R⁵ and R⁶ may be the same or different and represent (i) one or more hydrogen atoms, (ii) one or more halogen atoms, (iii) one or more C₁-C₆ alkyl groups optionally substituted with one or more halogen atoms, C₃-C₆ cycloalkyl groups, C₃-C₆ alkoxy-C₁-C₆-alkyl groups or phenyl groups, and

a represents 4.

3. The compound according to claim 1, which is represented by formula (I), wherein

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R¹ represents a chlorine atom,

R² represents a cyano group,

R⁴, R⁵ and R⁶ may be the same or different and represent (i) one or more hydrogen atoms, (ii) one or more halogen atoms or (iii) one or more C₁-C₆ alkyl groups optionally substituted with one or more halogen atoms, and

b represents 1.

4. A herbicide composition comprising a herbicidally effective amount of at least one compound according to claim 1.

5. The herbicide composition according to claim 4, further comprising a formulation assistant.

6. A method for controlling undesirable plants, comprising a step of applying an effective amount of at least one compound according to claim 1 to an undesirable plant or to a location of an undesirable vegetation.

7. A herbicide composition comprising a herbicidally effective amount of at least one compound according to claim 2.

8. A herbicide composition comprising a herbicidally effective amount of at least one compound according to claim 3.

9. The herbicide composition according to claim 7, further comprising a formulation assistant.

10. The herbicide composition according to claim 8, further comprising a formulation assistant.

11. A method for controlling undesirable plants, comprising a step of applying an effective amount of at least one compound according to claim 2 to an undesirable plant or to a location of an undesirable vegetation.

12. A method for controlling undesirable plants, comprising a step of applying an effective amount of at least one compound according to claim 3 to an undesirable plant or to a location of an undesirable vegetation.

13. A method for controlling undesirable plants, comprising a step of applying an effective amount of the herbicide composition according to claim 4 to an undesirable plant or to a location of an undesirable vegetation.

14. A method for controlling undesirable plants, comprising a step of applying an effective amount of the herbicide composition according to claim 7 to an undesirable plant or to a location of an undesirable vegetation.

15. A method for controlling undesirable plants, comprising a step of applying an effective amount of the herbicide composition according to claim 8 to an undesirable plant or to a location of an undesirable vegetation.

16. A method for controlling undesirable plants, comprising a step of applying an effective amount of the herbicide composition according to claim 5 to an undesirable plant or to a location of an undesirable vegetation.

17. A method for controlling undesirable plants, comprising a step of applying an effective amount of the herbicide composition according to claim 9 to an undesirable plant or to a location of an undesirable vegetation.

18. A method for controlling undesirable plants, comprising a step of applying an effective amount of the herbicide composition according to claim 10 to an undesirable plant or to a location of an undesirable vegetation.

* * * * *